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INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

Obtaining Nickel Hydroxide from Half-Products of Hydrometallurgical Processing of Nickel–Iron Batteries

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Abstract—The possibility of obtaining nickel hydroxide from solutions produced in ammonia leaching of the active paste of positive electrodes of a nickel–iron battery was studied.

One of widely occurring kinds of secondary nickel-containing raw materials in Russia is constituted by spent positive electrodes of nickel–iron batteries, which are processed by pyrometallurgical or hydro-metallurgical methods [1–3]. A possible scheme for processing of spent nickel–iron batteries includes treatment of the positive electrodes, based on the previously suggested [2] ammonia leaching to recover nickel without preliminary disassembly of lamellas. With the properly chosen processing conditions, the recovery of nickel into solution in this stage may be as high as 96–99%.

Nickel-containing process solutions can be used for further recovery of nickel and its compounds by various methods, e.g., by extraction with organic reagents, electrodeposition, hydrogen reduction, and crystallization in the form of neutral and double salts or nickel hydroxide [1].

In this study we examined the possibility of using ammonia leaching solutions to obtain pure nickel hydroxide, which is a valuable raw material for battery industry. Nickel(II) hydroxide was precipitated from ammonia leaching solutions containing sulfate ions [2] with a 4.85 M NaOH solution (density 1.18 g cm^{-1}). Preliminarily, a 100-ml portion of the solution was evaporated to a volume of approximately 25 ml, with a precipitate of a double complex salt of nickel formed at the end of evaporation. Then the volume was brought to 100 ml with water and the mixture was heated ($T \approx 70°C$), with the precipitate dissolving and the pH of the solution becoming 7. The resulting solution was placed in a buret, and the NaOH solution, in a microburet. The precipitation was performed under continuous agitation in a temperature-controlled ($T = 50°C$) 150-ml vessel. The alkali and ammonia solution were simultaneously introduced into the reaction volume (dropwise and as a flow, respectively), with their volume ratio maintained at 1 : (1–10) and the interval between addition of reagent portions (total volume of a portion 5–10 ml) equal to 10 min. After the last addition of alkali (pH 12), the reaction solution with a precipitate was kept with agitation for 90 min. The precipitate was allowed to settle for 120 min and filtered on a vacuum filter. Then the precipitate was washed with cold distilled water (~800 ml) and dried at 80°C for 120 min.

The precipitates obtained had light emerald to light green color, depending on the volume ratio of the reagent solutions added and on the uniformity of their introduction into the reaction volume. It was established that the optimal, as regards the filterability and homogeneity of the precipitates, ratio of the alkali and the ammonia solution is 1 : 5, with the best results obtained when this ratio is strictly maintained throughout the precipitation time. At the very beginning of the process, immediately after the addition of the first portions of the reagents, a finely dispersed well-agitated precipitate is formed in the reaction vessel. This precipitate can later be well filtered off; it has a light green color upon drying. If the volume ratio was shifted toward an excess (with respect to the optimal value) of an alkali, the precipitate became too dense and gave coarse clotted aggregates. At an excess of the ammonia solution, the precipitate dissolved and the solution acquired an emerald color and was poorly filterable; a dried precipitate had the form of shining crystalline scales of light emerald color. These specific features were the most pronounced in the initially made attempts to perform precipitation, when the ammonia solution was poured to an alkali solution or, in the opposite way, an alkali solution was poured to the ammonia solution. As already noted,

the optimal method is that of simultaneous mixing of the reagents in a prescribed volume ratio.

The X-ray diffraction pattern of the precipitate obtained from an ammonia–sulfate solution under the optimal conditions is shown in Fig. 1a. The peak positions are characteristic of nickel(II) hydroxide, which has a layered hexagonal crystal lattice of the CdI_2 type. It should be noted that the positions of the diffraction peaks and their relative intensities are in precise agreement with the tabulated data for pure nickel hydroxide, in contrast to those of the starting active paste (Figs. 1b, 1c), which also contain peaks corresponding to impurity phases. This fact confirms the efficiency of iron separation in the stage of nickel recovery by leaching from the spent active paste containing, on the average, 0.3–0.7 wt % Fe at 40–44 wt % Ni [2].

To assess the prospects for their possible utilization, the precipitates obtained from sulfate–ammonia leaching solutions were subjected to a comprehensive study.[1] The chemical analysis of the precipitates demonstrated that they contain (% relative to the initial mass): Ni 59–62, SO_4^{2-} 0.1–0.3, N <0.01, and Na <0.01. These data indicate that the precipitates contain only small amounts of water of crystallization and of main impurities. Figure 2 shows the results of an X-ray fluorescence microanalysis of the nickel hyroxide obtained. It can be seen that both the base elements (Ni and O) and trace impurities (Al, Si, S) are uniformly distributed over the precipitate particles. This indicates that the coagulation of particles in their nucleation and subsequent growth is uniform if the conditions specified above are satisfied. As the concentration of main impurities in the resulting nickel(II) hydroxide is low, it can be further used to obtain nickel salts.

An analysis of the size distribution of $Ni(OH)_2$ particles (Fig. 3a) demonstrated that particles of size 5–20 μm predominate in precipitates obtained under the optimal conditions. Precipitates of this kind have a specific surface area of about 1.6×10^3 $cm^2\,cm^{-3}$ and average pycnometric density of about 3.94 $g\,cm^{-3}$ (measured in a KOH solution of density 1.26 $g\,cm^{-3}$). Figure 3b shows an SEM pattern of nickel hydroxide particles. It follows from this figure that the precipitate is a dispersed system, with its separate particles having no pronounced crystal faceting and their shape being nearly spherical. These properties of the precipitates are of interest as regards their possible application as an electrode material for nickel–metal–hydride
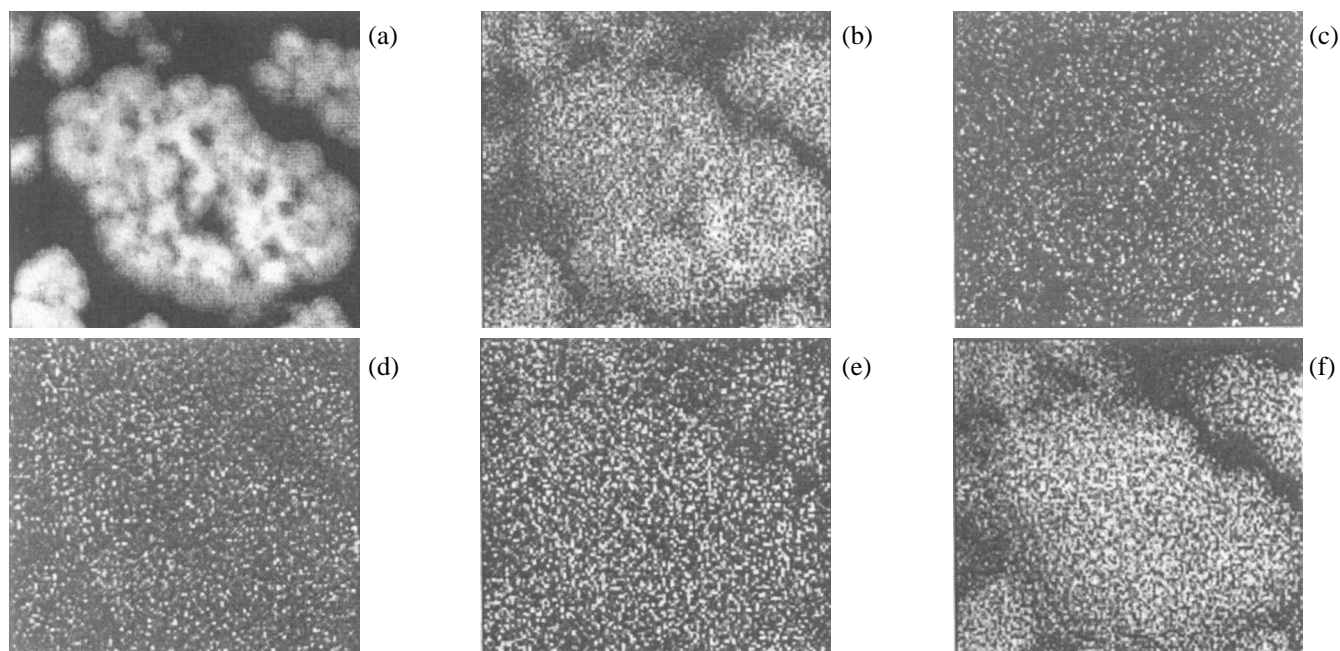
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[1] Studied at the Gipronikel' Research Institute (St. Petersburg).
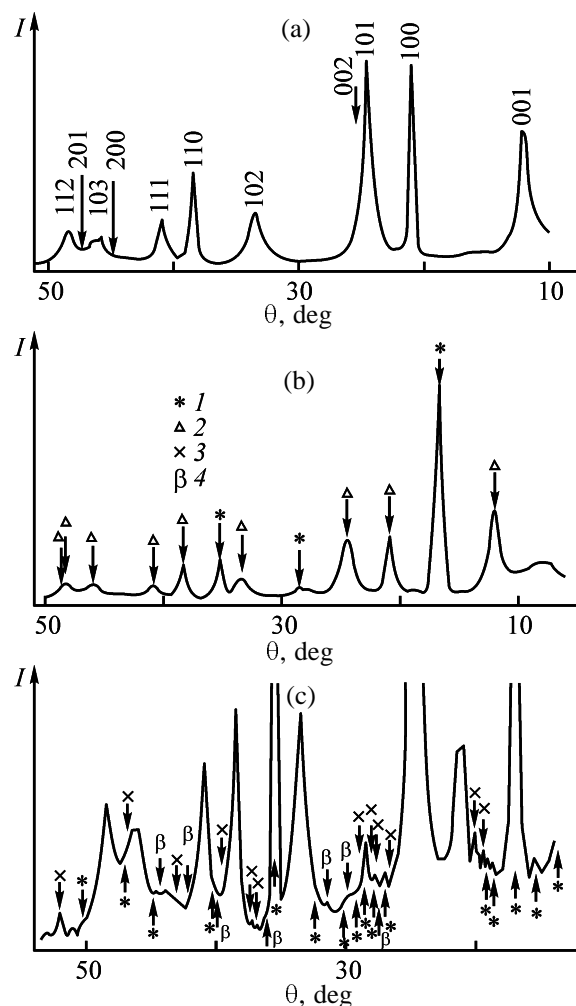
Fig. 1. X-ray diffraction patterns of (a) $Ni(OH)_2$ precipitate obtained upon addition of NaOH to sulfate–ammonia leaching solutions and (b, c) starting active paste of positive electrodes of nickel–iron batteries. FeK_α radiation. (θ) Bragg angle. Phase: (*1*) graphite, (*2*) $Ni(OH)_2$, (*3*) FeOOH, and (*4*) β-FeOOH.

batteries in which spherical nickel hydroxide is widely used.

The electrochemical properties of the material obtained were studied on electrodes fabricated by applying the paste on the current-carrying foamed-nickel support, with the subsequent drying and additional compaction. The substrate thickness before the additional compaction was 2.0 mm. The table lists the results obtained in measuring the discharge capacity of electrodes of this kind after the third charging–discharge cycle in comparison with the similar parameters of the electrodes fabricated from $Ni(OH)_2$ manufactured by OMG (Finland).

The data presented demonstrate that the nickel hydroxide precipitates obtained in this study compare

Fig. 2. Results of X-ray fluorescence microanalysis of the Ni(OH)$_2$ precipitate obtained by introduction of NaOH into sulfate–ammonia leaching solutions. (a) Image of a sample being analyzed; distribution of the intensity of the characteristic K_α radiation over this sample for (b) oxygen, (c) aluminum, (d) silicon, (e) sulfur, and (f) nickel.
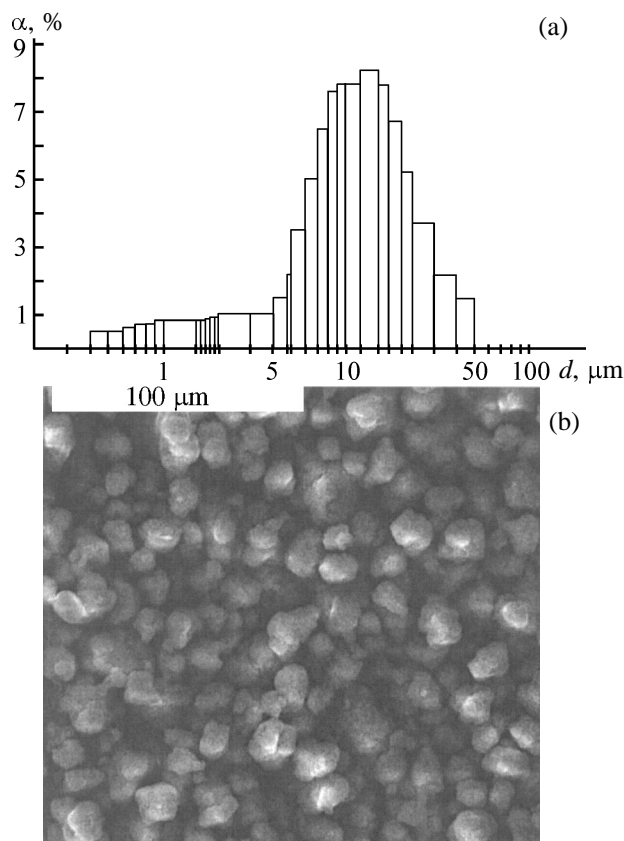
Fig. 3. (a) Size and (b) shape distribution s of Ni(OH)$_2$ particles obtained by introduction of NaOH into sulfate–ammonia leaching solutions. (α) Fraction of particles and (d) particle size.

well in their specific characteristics with the commercial material, being, however, looser, i.e., having a lower density, which leads to significant differences of the shape of the electrodes fabricated from these precipitates, compared to the presently existing samples. These facts suggest that, with the technology of Ni(OH)$_2$ precipitation from ammonia leaching solutions further optimized, it will be possible to improve the parameters of the precipitates obtained to values allowing their practical use.

CONCLUSIONS

(1) Pure nickel(II) hydroxide can be recovered from ammonia leaching solutions, which are half-products formed in hydrometallurgical processing of spent positive electrodes of nickel–iron batteries.

Electrochemical properties of electrodes based on OMG and Ni(OH)$_2$

Electrode material	Discharge capacity		Electrode thickness after additional compaction, mm	ρ_r,* g cm^{-1}
	A h g^{-1}	A h cm^{-3}		
OMG	0.22	0.55	~1.3	1.8
	0.24	0.57	~1.3	1.9
Ni(OH)$_2$	0.25	0.42	~0.47	0.7

* Density of rammed powder.

(2) Nickel(II) hydroxide obtained from ammonia leaching solutions containing sulfate ions can be used for subsequent production of pure nickel salts owing to the low content of the main impurities.

(3) Provided that the technology of its precipitation is further optimized, nickel(II) hydroxide obtained from ammonia–sulfate leaching solutions is of interest as a material for the active paste of electrodes of alkaline batteries.

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